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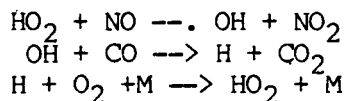
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PEROXY RADICAL DETECTION BY CHEMICAL AMPLIFICATION (PERCA)

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Important reactions of atmospheric free radicals are the chain oxidation of NO and CO. Thus:



In most models, the need to know the free radical concentration could also be described as the need to know the rate of the above oxidation chain in the atmosphere. It is the total rate of this chain (also carried by RO₂ and RO) which we measure using the PERCA. The PERCA is thus essentially a RO_x meter (with apologies to our geological colleagues). The PERCA works by adding excess CO (10%) and NO (5ppm) to a stream of air and measuring the NO₂ produced after 3s of reaction time. Since other processes produce NO₂, the chain reaction is modulated by switching the CO for N₂. The chain length is limited by the reaction OH + NO → HONO and is modeled to be somewhat over 1000. Measured chain lengths agree with the modeled numbers.

The instrument as presently configured weighs 35 lbs. and draws 1 amp. of 110v power. It uses cylinders of pure CO and 100 ppm NO in N₂. Measurements in the laboratory and in air at ground level have been made. In the laboratory sensitivity has been demonstrated to concentrations of total HO_x free radicals believed to be of order 10⁻³ ppb (~2.5 x 10⁴ cm⁻³). In the field, the high variable NO₂ background from NO₂ and O₃ + NO → NO₂ has limited sensitivity to 10⁸ cm⁻³.

All RO₂ radicals which react fast with NO to produce NO₂ are expected to be measured with equal sensitivity. Atmospheric PAN and HNO₄ are not an interference unless they decompose during the 3s reaction time. The effect of that interference has been modeled, but not yet measured. Fortunately, it is self-limiting. At high temperatures decomposition is faster in the cell, but, for the same reason, under most circumstances, at higher temperatures, there is expected to be less PAN and HNO₄ in the atmosphere.

Bibliography:

"Measurement of Atmospheric Peroxy Radicals by Chemical Amplification", C.A. Cantrell, D.H. Stedman, and G.J. Wendel, Analyt. Chem. **56**, 1496, 1984.

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"Laboratory Studies of an HO₂/RO₂ Detector", D.H. Stedman and C.A. Cantrell. Proceedings of the AMS Conference on Non-Urban Troposphere, Williamsburg, VA., May, 1982.

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Comments

The concern by the workshop participants about this method was directed to its lack of specificity and, under some conditions, the stability of the chemical amplification employed.